

Effect of Molybdenum on the Corrosion Behavior of Amorphous Fe-Mo-C alloys in 1N HCl

著者	HASHIMOTO Koji, ASAMI Katsuhiko, NAKA Masaaki, MASUMOTO Tsuyoshi
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	27
page range	237-245
year	1979
URL	http://hdl.handle.net/10097/28081

Effect of Molybdenum on the Corrosion Behavior of Amorphous Fe-Mo-C alloys in 1 N HCl*

Koji HASHIMOTO, Katsuhiko ASAMI, Masaaki NAKA
and Tsuyoshi MASUMOTO

The Research Institute for Iron, Steel and Other Metals

(Received January 31, 1979)

Synopsis

The addition of molybdenum to amorphous Fe-18C alloy results in passivation by anodic polarization even in 1N HCl. However, its addition in a large amount increases the anodic current density in both the active and passive regions and lowers the corrosion potential. X-ray photo-electron spectroscopy was used to determine the correlation between the composition of surface film and the corrosion resistance of alloys. The alloying with a proper amount of molybdenum facilitates the formation of molybdenum-enriched surface film as a result of active dissolution and hence assists the passivation by the formation of passive hydrated iron oxy-hydroxide film. However, the excess addition of molybdenum leads to an excess increase in the anodic activity of alloys and accordingly is not greatly effective for increasing the corrosion resistance.

I. Introduction

It is well known for many years that the addition of molybdenum to stainless steels improves their resistance to attack by chloride and acid solutions. Many investigators in describing the beneficial effect of molybdenum have stated that molybdenum increases the thickness of passive films on the steels^(1,2) and changes the protective quality of the passive films by including molybdenum⁽²⁻⁵⁾. However, according to Lumsden *et al.*^(6,7) Auger electron spectroscopic study has revealed the fact that the improved corrosion resistance obtained by the addition of molybdenum cannot be explained by its enrichment in the protective film. Some of the present authors^(8,9) in reporting X-ray photo-electron spectroscopic and electrochemical studies of ferritic stainless steels have shown that the addition of molybdenum does not change the thickness and composition of passive film but

* The 1694th report of the Research Institute for Iron, Steel and Other Metals.

- (1) A.P. Bond and E.A. Lizlovs, *J. Electrochem. Soc.*, **115** (1968), 1130.
- (2) K. Sugimoto and Y. Sawada, *Corros. Sci.*, **17** (1977), 425.
- (3) T.N. Rhodin, *Corrosion*, **12** (1956), 465.
- (4) N.A. Nielsen and T.N. Rhodin, *Z. Electrochem.*, **62** (1958), 707.
- (5) T. Kodama and J.R. Ambrose, *Corrosion*, **33** (1977), 155.
- (6) J.B. Lumsden and R.W. Staehle, *Scr. Metall.*, **6** (1972) 1205.
- (7) A.E. Yaniv, J.B. Lumsden and R.W. Staehle, *J. Electrochem. Soc.*, **124** (1977), 490.
- (8) K. Hashimoto, K. Asami and K. Teramoto, *Corros. Sci.*, **19** (1979), 3.
- (9) K. Hashimoto and K. Asami, *Corros. Sci.*, **19** (1979).

decreases the active dissolution rate of steels and hence assists the formation of passive hydrated chromium oxy-hydroxide film.

On the other hand, the addition of molybdenum to iron decreases the passivation tendency of iron in 1 N H_2SO_4 because of transpassive reaction of molybdenum⁽²⁾. Furthermore, binary Fe-Mo alloys show a single anodic polarization curve of active dissolution in 1 N HCl, not showing passivation⁽²⁾. Nevertheless, the present authors have found that amorphous Fe-Mo-13P-7C alloys passivate in 1 N HCl⁽¹⁰⁾ by forming a passive hydrated iron oxyhydroxide film⁽¹¹⁾.

A recent study by some of the present authors⁽¹²⁾ has revealed the fact that the addition of molybdenum to amorphous Fe-C alloy also increases its corrosion resistance and leads to the passivation in 1 N HCl by anodic polarization. The work reported hereafter has been undertaken to clarify the role of molybdenum in improving the corrosion resistance of amorphous Fe-Mo-C alloys. X-ray photoelectron spectroscopy has been used to determine the composition of surface film formed on the alloys as a function of polarization potential.

II. Experimental procedure

Amorphous Fe-Mo-18C alloys were prepared by a rotating wheel method. The number attached to respective element in an alloy formula denotes the nominal content in atomic percent.

A solution employed was 1 N HCl which was open to the air. Polarization measurements were made by a potentiodynamic method with a potential sweep rate of $2.37 \times 10^{-3} \text{ V} \cdot \text{s}^{-1}$, starting from the corrosion potential at room temperature. The specimens for X-ray photo-electron spectroscopic measurements were prepared by anodic polarization for 3600 s at various constant potentials, followed by rinsing with de-ionized water and dried by air blasting.

X-ray photo-electron spectra were measured by AEI-ES 200 electron spectrometer with Mg $\text{K}\alpha_{1,2}$ excitation (1253.6 eV). Binding energies of electrons were determined by a calibration method described elsewhere^(13,14). The simultaneous determination of the composition and thickness of surface film and the composition of underlying substrate alloy was performed by the same method as reported in previous papers^(15,16) by using integrated intensities of Fe 2p_{3/2}, Mo 3d, Cl 2p, O 1s and C 1s spectra. Prior to the composition analysis the Fe 2p_{3/2} and Mo 3d spectra were separated to those corresponding to oxidized and metallic states, and individual integrated intensities were obtained. The O 1s spectrum was also

(10) M. Naka, K. Hashimoto and T. Masumoto, *J. Non-Cryst. Solids*, **29** (1978), 61.

(11) K. Hashimoto, M. Naka, K. Asami and T. Masumoto, *Corros. Sci.*, **19** (1979).

(12) M. Naka, K. Hashimoto and T. Masumoto, *J. Non-Cryst. Solids*, **30** (1979).

(13) K. Asami, *J. Electron Spectrosc.*, **9** (1976), 469.

(14) K. Asami and K. Hashimoto, *Corros. Sci.*, **17** (1977), 559.

(15) K. Asami, K. Hashimoto and S. Shimodaria, *Corros. Sci.*, **17** (1977), 713.

(16) K. Asami, K. Hashimoto and S. Shimodaria, *Corros. Sci.*, **18** (1978), 151.

separated to OM oxygen (metal-O-metal bond with a low binding energy peak) and OH oxygen (metal-OH and metal-OH₂ bonds with a high binding energy peak)^(14,17). Previously reported values^(14,15,18) of photo-ionization cross-sections relative to the O 1s electrons were used for quantitative determination.

III. Results

Fig. 1 shows anodic polarization curves of amorphous Fe-Mo-18C alloys measured in 1 N HCl. These alloys exhibit complicated active dissolution curves. The first peak has been found on amorphous Fe-13P-7C⁽¹⁰⁾ and Fe-20B⁽¹⁹⁾ alloys containing various metallic elements and corresponds to the active dissolution of alloys. The second peak at about 0.3 V (SCE) has appeared for amorphous Fe-Mo-13P-7C alloys with an increase in molybdenum content⁽¹⁰⁾ and accordingly may result from transpassive dissolution of molybdenum. The Fe-Mo-18C alloys

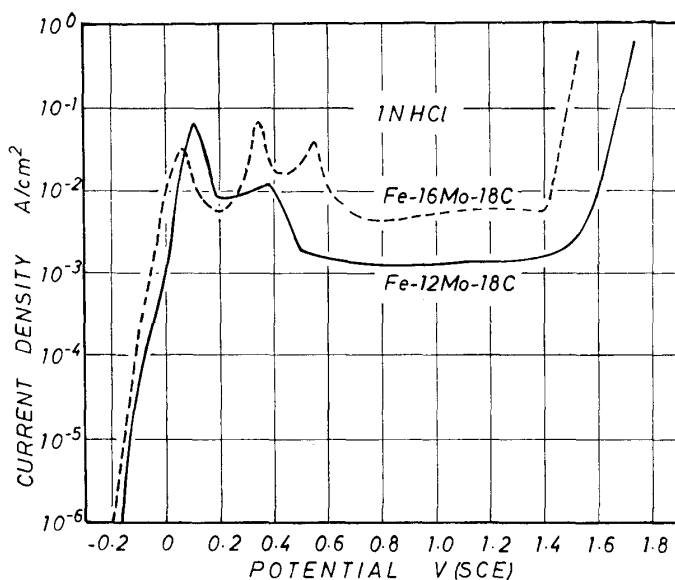


Fig. 1. Potentiodynamic anodic polarization curves of amorphous Fe-12Mo-18C and Fe-16Mo-18C alloys measured in 1 N HCl.

tend to passivate by anodic polarization, not showing an abrupt rise in current density due to pitting up to transpassive region of iron. The addition of molybdenum seems responsible for the anodic passivation because crystalline iron⁽²⁾ and amorphous Fe-13P-7C⁽¹⁰⁾ and Fe-20B⁽¹⁹⁾ alloys without molybdenum do not passivate anodically in 1 N HCl. The amorphous Fe-Mo-13P-7C alloys have revealed the fact that an increase in molybdenum content raises the corrosion potential

(17) K. Asami, K. Hashimoto and S. Shimodaira, *Corros. Sci.*, **16** (1976), 35.

(18) K. Teramoto, K. Asami and K. Hashimoto, *Corros. Engng. (Boshoku Gijutsu)*, **27** (1978), 57.

(19) M. Naka, K. Hashimoto and T. Masumoto, *J. Non-Cryst. Solids*, to be published.

and lowers the anodic current density in both the active and passive regions⁽¹⁰⁾. Similarly, the increase in molybdenum content up to 12 at.% has increased the corrosion resistance of amorphous Fe-Mo-18C alloys⁽¹²⁾. Conversely, the present result exhibits the fact that the increase in molybdenum content from 12 to 16 at.% lowers the corrosion potential and raises the current density except the current density at the first peak. These changes of polarization curves have been observed for a series of amorphous Fe-Mo-18C alloys⁽¹²⁾. Accordingly, the addition of an adequate amount of molybdenum favors the anodic passivation but the addition in a large amount decreases the corrosion resistance of Fe-Mo-18C alloys. In addition, the current density of Fe-Mo-18C alloys containing 12 at.% or less molybdenum is more than one order of magnitude as high as that of Fe-Mo-13P-7C alloys.

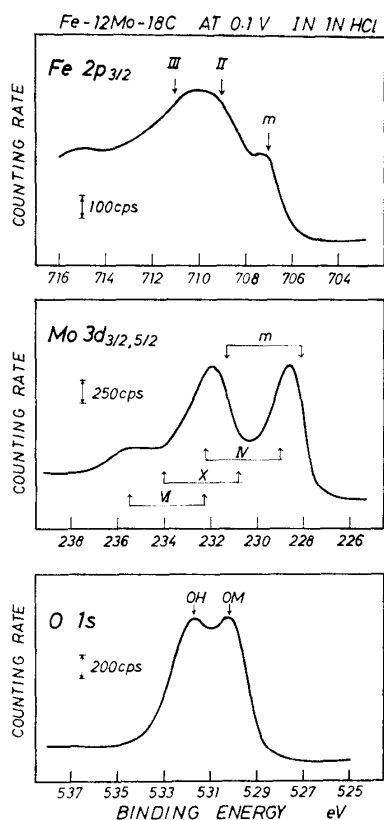


Fig. 2. X-ray photo-electron spectra measured from amorphous Fe-12Mo-18C alloy polarized potentiostatically for 3600 s at 0.1 V (SCE) in 1 N HCl. Arrows indicate the peak positions of photoelectrons from metallic (m) and oxidized states of Fe and Mo and from OH and OM oxygen. The valence of cation is described by Roman numeral except Mo^{X} which is assumed to be close to Mo^{V} ⁽²⁰⁾.

X-ray photo-electron spectra were measured for the specimens polarized potentiostatically. Fig. 2 shows examples of spectra. As can clearly be seen the Fe $2p_{3/2}$ spectrum consists of two peaks corresponding to the metallic state in an underlying alloy at a low binding energy and the oxidized state in a surface film at a high binding energy. The high binding energy peak is further composed of those for ferrous and ferric states^(14,17). The Mo 3d spectrum is very complicated by superposition of $3d_{3/2}$ and $3d_{5/2}$ electrons from various states. Because of the intense signal from tetravalent molybdenum, the signal from metallic state is

not separated from the signal of tetravalent molybdenum. The middle peak consists mainly of $3d_{3/2}$ electrons from tetravalent state and $3d_{5/2}$ electrons from hexavalent state. The latter state gives a $3d_{5/2}$ signal at a high binding energy. The high intensity at the saddle between peaks of $3d_{5/2}$ and $3d_{3/2}$ electrons from hexavalent molybdenum suggests the existence of another molybdenum cation whose valence X has been assumed to be close to five⁽²⁰⁾. The O 1s spectrum shows two peaks which arise from OM oxygen and OH oxygen. Chloride, which gave the Cl 2p signal at about 198.9 eV, was also found in the surface film.

Figs. 3 and 4 show analytical results of composition of surface film as a function of polarization potential. Fig. 3 reveals the cationic fraction of molybdenum in the surface film. Molybdenum is highly enriched in the surface film formed in

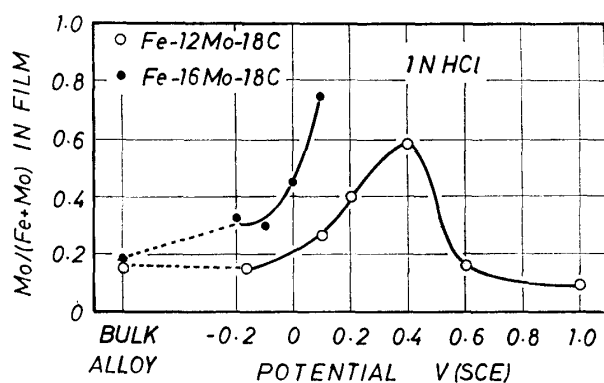


Fig. 3. Cationic fraction of molybdenum in the surface film formed on amorphous Fe-12Mo-18C and Fe-16Mo-18C alloys by potentiostatic polarization at various potentials for 3600 s in 1N HCl. Included in the figure for comparison is the ratio of molybdenum to the sum of iron and molybdenum in bulk alloys.

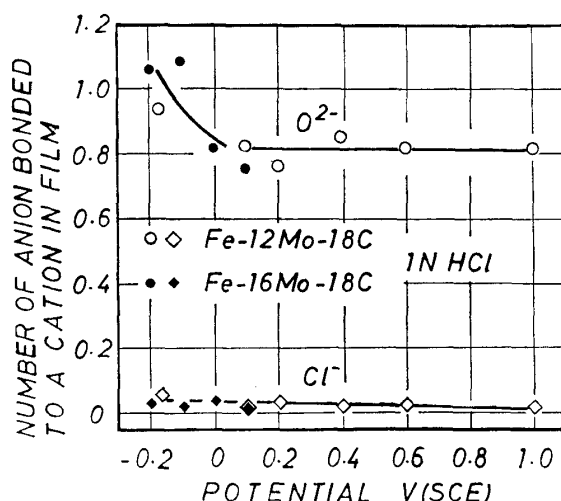
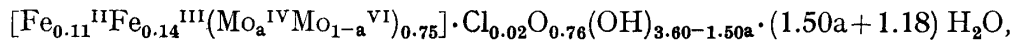


Fig. 4. Numbers of O^{2-} and Cl^- ions bonded to a cation in the surface film of the same specimens as those described in Figure 3.

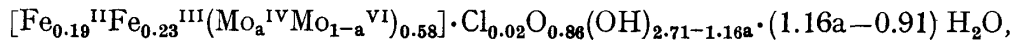
(20) K.S. Kim, W.E. Baitinger, J.W. Amy and N.W. Winograd, *J. Electron Spectrosc.*, 5 (1974), 351.

the active region of alloys but is not concentrated in the passive film. This change in the molybdenum content in the surface film with potential is in good agreement with the results obtained for the surface films formed on 30Cr-2Mo ferritic stainless steel⁽⁸⁾ and amorphous Fe-Mo-13P-7C alloys⁽¹¹⁾ in 1 N HCl, although the molybdenum content of the passive film on Fe-Mo-18C alloys is fairly higher than that on Fe-Mo-P-C alloys. Fig. 4 shows average numbers of O²⁻ and Cl⁻ ions bonded to a cation as a function of polarization potential. O²⁻ corresponds to OM oxygen. The content of O²⁻ in the film is nearly constant except that in the film formed at low potentials. The chloride content in the film is fairly low and tends to decrease with an increase in polarization potential. The surface film further contains OH⁻ ion and bound water (H₂O). The average number of OH⁻ ion bonded to a cation is usually estimated as the negative charge necessary for neutralization of positive charge remaining after subtraction of negative charges of O²⁻ and Cl⁻ ions from the positive charges of all cations in the film. However, because the ratio of various molybdenum cations cannot be determined, the amounts of OH⁻ ion and bound water are not distinguished from each other. The average compositions of surface films can be expressed as follows:

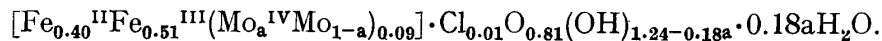
Surface films formed in the active region
on Fe-16Mo-18C alloy at 0.1 V (SCE)



on Fe-12Mo-18C alloy at 0.4 V (SCE)



the passive film on Fe-12Mo-18C at 1.0 V (SCE)



It can, therefore, be said that the passive film formed on the amorphous Fe-Mo-18C alloy consists mainly of hydrated iron oxy-hydroxide which is the same as the passive films formed on iron and low chromium-iron alloys in 1 N H₂SO₄⁽¹⁶⁾.

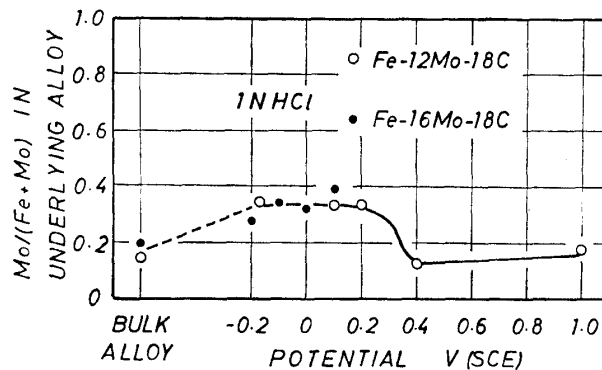


Fig. 5. The ratio of molybdenum to the sum of iron and molybdenum in the alloy immediately under the surface film whose composition is shown in Figures 3 and 4. The corresponding ratios of bulk alloys are included in the figure for comparison.

Fig. 5 shows the atomic ratio of molybdenum to the sum of iron and molybdenum in the alloy immediately under the surface film. The active dissolution of alloys, which leads to the molybdenum enrichment in the surface film, results also in the enrichment of metallic molybdenum in the surface region of underlying alloys. However, the molybdenum content of the surface region of alloy under the passive film is nearly the same as that of bulk alloy. Carbon contained in the alloys gave a shoulder on the low binding energy side of main peak from contaminant hydrocarbon. If one assumes that carbon distributes uniformly in the underlying substrate alloys, the atomic fraction of carbon in the alloys after polarization goes up to over 0.3 in contrast to the bulk composition of 0.18.

IV. Discussion

In general, the addition of molybdenum to stainless steels^(8,9) and amorphous alloys⁽¹⁰⁾ decreases their anodic current densities in both the active and passive regions and increases the pitting resistance of stainless steels. The beneficial effect of molybdenum for improving the resistance to attack by chloride and acid solutions has been interpreted by some of the present authors^(8,9) as follows: Because the dissolution rate of molybdenum is slower than other constituents of iron-base alloys in the active region of alloys, the active dissolution results in the formation of molybdenum-enriched corrosion product film on the alloy surface. This fact leads to the decrease in the open circuit corrosion rate and anodic current density in the active region. Similarly, when polarization is made to the passive region, the instantaneous initial active dissolution necessary prior to the formation of passive film results in the formation of molybdenum-enriched surface film. This film inhibits further active dissolution of alloys and hence favors the formation of passive film.

In the present work the amorphous Fe-Mo-18C alloys passivate anodically in 1 N HCl by forming a passive hydrated iron oxy-hydroxide film which is the same as the passive film formed on iron in 1 N H₂SO₄, despite the fact that the passivation of iron is impossible in 1 N HCl. In addition, when the molybdenum content of the surface film is higher, the first peak of anodic polarization curve is lower. These results seem to substantiate the interpretation of the role of molybdenum mentioned above.

However, the present work reveals the fact that the addition of molybdenum in a large amount to amorphous alloys is rather detrimental. Molybdenum is more active than iron. Accordingly, the addition of molybdenum to iron-base alloys more or less increases their anodic activity. The high anodic activity, on the one hand, provides the rapid supply of molybdenum to form the molybdenum-enriched surface film. On the other hand, the corrosion behavior of alloys is sometimes determined by the anodic activity of alloys unless the protective quality of surface film is sufficiently high. This seems responsible for the increase in anodic

current density with the excess addition of molybdenum. In addition, the passivation of iron-molybdenum alloys takes place not by the formation of molybdenum species but by the formation of iron oxy-hydroxide, since the molybdenum species are unstable in the passive region of alloys especially in acidic solutions due to the trans-passive reaction of molybdenum. Consequently, the passivation of iron-molybdenum alloys becomes difficult with the excess addition of molybdenum.

When the active dissolution slows down by passivation the molybdenum-enriched film formed through the rapid supply of molybdenum due to the active dissolution dissolves out into solutions. Accordingly, molybdenum is generally deficient in the passive film formed on iron-base alloys in acidic solutions^(8,9,11). However, the passive film formed on Fe-Mo-18C alloy contains unstable molybdenum species in a higher amount in comparison with the passive film formed on Fe-Mo-13P-7C alloys in 1 N HCl⁽¹¹⁾. In addition, the corrosion rate and anodic current density of Fe-Mo-18C alloys are higher than those of Fe-Mo-13P-7C alloys⁽¹⁰⁾. The present authors⁽²¹⁾ in reporting the effects of metalloids on the corrosion behavior of amorphous iron-base alloys have stated that phosphorus added to alloys is most effective for increasing the active dissolution rate of alloys and leads to the enrichment of beneficial species with a high protective quality at the alloy-solution interface and to the passivation of alloys. In the present work the specimens contain a large amount of carbon after anodic polarization. Carbon is thermodynamically more stable than iron and molybdenum, particularly in the active region of alloys, and may preferentially remain on the alloy surface as a result of rapid dissolution of alloys. In addition, carbon contained in amorphous iron-base alloys does not effectively accelerate the active dissolution of alloys. It can, therefore, be said that, when only carbon is contained as a metalloid in amorphous iron-molybdenum alloys, the enrichment of iron species which is necessary for the passivation of the alloys is not sufficient at the alloy-solution interface and hence incomplete passivation occurs by the formation of film including unstable molybdenum species.

V. Conclusion

The amorphous Fe-Mo-18C alloys passivate by anodic polarization in 1 N HCl, not suffering pitting corrosion up to the transpassive region of iron. However, the addition of molybdenum in a large amount increases the anodic current density in both the active and passive regions.

The surface films formed were examined by X-ray photo-electron spectroscopy as a function of polarization potential. The surface film formed in the active region of alloy contains a large amount of molybdenum, while the passive film consists mainly of hydrated iron oxy-hydroxide.

(21) K. Hashimoto, M. Naka, K. Asami and T. Masumoto, *Corros. Engng. (Boshoku Gijutsu)*, **27** (1978), 279.

The addition of an adequate amount of molybdenum favors the formation of molybdenum-enriched surface film as a result of active dissolution of alloy. This fact decreases the active dissolution rate of alloy and assists the formation of passive hydrated iron oxy-hydroxide film. However, its excess addition leads to an excess increase in anodic activity of alloys and is not greatly effective for increasing the corrosion resistance in comparison with its adequate addition.